A Hot-Recycled-Solid Oil Shale Retorting Process For The Production of Shale Oil and Specialty Chemicals

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ABSTRACT

At Lawrence Livermore National Laboratory, we are studying Hot-Recycled-Solid (HRS) oil shale retorting processes through a series of fundamental studies, operation of a 4 tonne-per-day HRS pilot plant and development of an Oil Shale Process (OSP) mathematical model. Over the last two years, under an industrial CRADA with four major oil companies[1], we have completed a series of runs (H10 - H27) using the pilot plant to demonstrate the technical feasibility of the technology, maintain and enhance the knowledge base gained over the past two decades through research and development and determine the follow on steps needed to advance the technology towards commercialization.

The pilot plant, which features no moving parts in critical areas, has been successfully operated for over 100 hours, demonstrating ease of control and reliability of the process. Efficiency is obtained via high throughput, thorough carbon utilization, waste shale heat recovery, improved oil yield and one hundred percent utilization of mined material, including shale fines. We have demonstrated the ability to work with both lean and rich shales (22 - 38 gallons-per-ton), and environmentally the process has superior behavior producing non-hazardous waste shale, minimal sulfur emissions, lower NOx emissions and minimum CO_2 production.

Fundamental laboratory experiments support the pilot plant efforts with determination of kinetics for pyrolysis, combustion and carbonate decomposition for the process as well as determining specifications for produced raw shale oil. In addition, we have developed the Oil Shale Process (OSP) model to aid in critical thinking and scale up of the HRS process.

We have put forth a commercial plant concept which combines the production of refined shale oil, meeting motor fuel specifications, with electric power and specialty chemical production. This plant concept would fully utilize available thermal energy, would solve the waste shale cooling problem and would produce a revenue stream through power and specialty chemical sales which would greatly offset plant operating costs. The net result would be a plant at modest scale (10,000 barrels per day) producing fifty percent specialty chemicals and fifty percent refined motor fuel product[2]. Under this scenario, the motor fuel price required to provide a fifteen percent rate of reutrn on investment would be 71 cents per gallon, which equals the average wholesale price of motor fuel in 1993.

INTRODUCTION

The oil shale deposits in the Western US represent a massive liquid fuel resource, with over 600 billion barrels of recoverable deposits in the Piceance Basin alone. Our objective, together with our CRADA partners, is to demonstrate advanced technology that could lead to an economic and environmentally acceptable commercialization of oil shale.

We have investigated the technical and economic barriers facing the introduction of an oil shale industry and we have chosen Hot-Recycled-Solid (HRS) oil shale retorting as the primary advanced technology of interest. We are investigating this approach through fundamental research, operation of a 4 tonne-per-day HRS pilot plant and development of an Oil Shale Process (OSP) mathematical model.

Over the last three years, from June 1991 to June 1993, we completed a series of runs (H10 - H27) using the 4-TPD pilot plant to demonstrate the technical feasibility of the HRS process and answer key scale-up questions. With our CRADA partners, we seek to further develop the HRS technology, maintain and enhance the knowledge base gained over the past two decades through research and development by Government and industry and determine the follow on steps needed to advance the technology towards commercialization.

One of the crucial challenges in beginning a oil shale industry is how to overcome the high capital cost and long lead time needed to make process improvements which would enable shale oil to compete as a fuel feed stock. We have chosen to focus on an initial plant that converts a large

[1] Cooperative Research and Development Agreement, established in February 1992 with Amoco, Chevron, Conoco and Unocal
[2] A mixture of fuels, thirty percent each motor and aviation gasoline and forty percent diesel fuel.

fraction of its production into high-valued specialty products to gain an initial market entry. We have determined the economics for a plant producing 10,000 Bbl/day of oil from shale. The plant converts the raw shale oil into a slate of high valued products including specialty chemicals, a shale oil modified asphalt binder and transportation fuels, while co-producing electric power. This small scale venture is shown to be competitive in today's market with a fifteen percent internal rate of return on a capital investment of $725 million dollars. Once in operation, expansion to 50,000 Bbl/day has the potential to become economic through economies-of-scale and cost reductions based on operating experience and plant innovation. This small beginning would provide the operating experience prerequisite for a larger industry, if and when appropriate, that could supply a significant fraction of the US liquid transportation fuel needs.

PROJECT DESCRIPTION

The LLNL 4-tonne-per-day pilot plant consists of a circulating loop and peripheral equipment for the production of oil from shale. Major units of the facility include a fluidized bed mixer, a moving packed bed pyrolyzer, a pneumatic lift pipe and a fluidized bed combustor. Solids are circulated around the loop at 10 kg/min. Fresh shale, crushed to a top size of 7mm, is mixed with hot circulating solids in the fluidized bed mixer. Rapid pyrolysis occurs in 2-3 minutes as the shale passes through the mixer and moving packed bed pyrolyzer. Produced oil vapor, containing water and dust pass through cyclones and filters prior to staged cooling for product recovery. Residual carbon on the spent shale, after pyrolysis, is combusted in the pneumatic lift pipe and fluidized bed combustor, providing the process heat, completing the circulation loop.

Solid flow and bed levels within the circulating loop are maintained using a pair of L-valves, one located below the pyrolyzer and one located below the fluidized bed combustor. Each valve is equipped with a horizontal skid separating inlet and exit by approximately 10 inches. Solids are transported from inlet to exit using gas jets which are pulsed at a frequency of once every 1 to 2.5 seconds. Each pulse moves approximately 250 grams of material. By adjusting the pulse rate and local pressure in the vicinity of the L-valve we achieve a balanced loop at the designed circulation rate, processing 2.5 kg/min of raw shale.

Concurrent to our pilot plant studies is the development of a steady state OSP mathematical model. OSP models each of the major components of the process, allowing us to compute properties and phenomena not readily determined experimentally. The model serves as a critical judge of the experiments and an aid in process scale up. One of the major discrepancies early on between model and experiment was the degree of carbonate decomposition which occurred. To resolve this discrepancy, we have, in the laboratory, reexamined carbonate decomposition kinetics, focusing on the lower temperature ranges typical of our retorting conditions.

OIL SHALE PROCESS MODEL (OSP) RESULTS

We continue to develop our Oil Shale Process model (OSP) as a aid toward process scale up and critical thinking concerning our pilot plant results[1]. OSP is a steady state model, written in FORTRAN, which allows a variety of modules to be coupled together to simulate some overall process. The model consists of three interacting parts: a control portion which handles overall direction of computation and is responsible for coupling process units together through the use of stream variables; a service routine portion which allows common properties to be computed; and any number of modules which do the actual computations associated with a given unit operation. The model defines three types of streams: solid, gas and liquid. All streams have associated with them values for composition, temperature and flow rate. Solid streams are treated as a homogeneous collection of a single specified particle size. Multiple particle sizes are handled by specifying multiple solid streams.

OSP currently contains 13 computational modules. These modules have been kept relatively simple but allow many of the important oil shale physical and chemical processes to be modeled. The modules rely on one of two simplifying assumptions, either one-dimensional co-current flow or complete mixing. The one-dimensional co-current flow construct allows particle/gas systems to be modeled, such as a dense phase moving packed bed, or a dilute phase lift-pipe. The complete mixing construct has utility in modeling fluidized bed systems. Using some combination of these two module types, a variety of unit operations can be simulated.

The moving packed bed pyrolyzer provides a good example of how OSP operates. In this unit, the solids travel from top to bottom in plug flow, while a sweep gas and vapors produced in the bed travel radially from centerline to wall, where vapor removal ports are located. This non co-current gas solid contact is modeled within OSP as a series of well mixed modules coupled from top to bottom to simulate the solid motion.

Under most circumstances, pilot plant results are uses as a guide in verifying modeling assumptions. However, in one case, the discrepancy between model and pilot plant could not be rectified by altering model constructs. This was the case for the measured amount of carbonate decomposition observed from the pilot plant.

LABORATORY EXPERIMENTAL RESULTS

We have recently published retorts of fundamental laboratory experiments in oil coking kinetics[2], char combustion kinetics[3] and flue gas NOx reduction with ammonia addition[4]. Our latest laboratory study focused on carbonate decomposition kinetics.

Decomposition kinetics were measured in the laboratory as an aid in resolving the discrepancy between model and experiment. In the experiments, raw shale was first prepared via slow combustion at low temperature (200 to 350 °C) to remove all of the kerogen while not affecting the initial mineral carbonate concentrations. The prepared sample was then dropped into a fluidized bed and the temperature was ramped from initially 500 °C to 850 °C at 5 deg/min. The evolved CO_2 was measured on a mass spectrometer as a determinate of the rate of carbonate decomposition. Analysis of the dropped sample showed 96% of the carbon to be inorganic. A first order kinetic expression was fit to the experimental data. The kinetics were faster, particularly at low temperatures, compared to previously reported results used in the OSP model. Incorporating these kinetics into OSP has eliminated the large discrepancy between model and experiment.

ECONOMICS AND COMMERCIALIZATION RESULTS

Our commercial concept for the HRS process combines reliability and efficiency with the production of high valued products and minimum environmental disruption. Economics for a 10,000 Bbl/day plant producing a slate of high valued products and co-producing electric power is discussed below.

Development of an efficient, reliable retorting process coupled with pioneering efforts by others in using shale oil as a chemical feed stock for the manufacture of high valued specialty chemicals and for use as an asphalt binder, using the Shale Oil Modified Asphalt (SOMAT)[3] process combine to make for a small scale venture potentially profitable in today's market.

The heart of the 10,000 Bbl/day commercial HRS process is very similar to a combined cycle circulating bed boiler for power production. In this plant, raw shale would first be pyrolyzed to produce oil, followed by combustion of residual carbon to produce thermal energy to drive the process and electric power for on-site use and off-site sale. The power cycle provides a means for spent shale cooling and fuel gas utilization while providing enough revenue to offset the cost of mining the raw shale.

The produced shale oil is split into three fractions. Ten percent is converted into specialty chemicals, unique to shale oil, which could command a sale price of $100/Bbl. The heaviest forty percent is converted into an asphalt binder (SOMAT) for road paving, with a projected sale price of $100/Bbl. The lightest fifty percent is then hydrotreated/refined producing a slate of transportation fuel products ranging from diesel to aviation fuel. The wholesale market price for this transportation fuel mix, averaged in 1993, $.73/gallon or $31/Bbl.

The economics of this 10,000 Bbl/day plant are shown in Table 1. Cost and revenue items are reported on per capacity basis, assuming a 330 day operating year. The capital cost on the $725 million dollar plant with a 15 percent internal rate of return (IRR) on investment equals a capital charge of $37/Bbl. Operating costs including mining, disposal, plant operations and maintenance are estimated by direct comparison with Unocal's operating experience at Parachute Creek. These costs are estimated at $23/Bbl. Hydrotreating/refining costs of $10/Bbl are also based on Unocal's experience, with fifty percent of the product needing hydrotreating in the current plant configuration, this equates to a $5/Bbl cost. The next two operating costs involve conversion of forty percent of the product into a shale oil modified asphalt binder SOMAT and ten percent into specialty chemicals.

Next in the table are the four products from the plant. The first is excess electrical production capacity obtained from the cooling the waste shale and on-site combusting of produced fuel gas. Off-site electrical sales amount to a $5/Bbl credit. The sale of SOMAT and specialty chemicals, each assumed to have a value of $100/Bbl bring in an additional $50/Bbl revenue, leaving a $15/Bbl gap between costs and revenues, with fifty percent of the product left. Here the table deviates from the heading by reporting the required price of the transportation fuel products needed to achieve the fifteen percent rate of return desired. As shown, the required price is about equal to the wholesale price of these fuels during 1993. Thus, the economics for a 10,000 Bbl/day plant have been shown to provide a fifteen percent rate of return on investment in today's market.

Table 2 shows the impact of scale up on economics. As more capacity is added, the capital and operating costs per barrel decline, while revenues from the production of high valued specialty products decline. The required motor fuel price increases to $39/Bbl or $.93/gallon to achieve the desired fifteen percent rate of return, which is a foreseeable rise in fuel price over the next 1-2 decades. In addition, process improvements and innovation based on experience will aid in lowering the overall cost projections for this plant.

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[3] The New Paraho Corporation, Aurora, Colorado.

CONCLUSIONS

Oil shale is one of the most promising alternatives to dwindling petroleum supplies in the US, with over 600 billion barrels of recoverable deposits in the Piceance Basin of Colorado alone. A commercial industry would provide domestic feed stock for specialty chemicals, asphalt binders for longer lasting roads, alternative transportation fuel and electric power at a cost competitive in today's market. A demonstrated technology would provide domestic jobs, aid the US balance-of-payments and give a measure of energy security by serving to cap the price of imported oil and provide an option to partially replace foreign oil in an extended national emergency.

A small-scale industry, today, exploiting high valued products would provide the framework for technological advancement to bringing down the cost for a potential large-scale fuels industry tomorrow. The Government owns most of the resource, and stands to benefit from a commercial oil shale industry through lease and tax revenues. Technical development, however, has been left to industry, with the cost of development proving to be too large for any single company to bear. A small investment by Government, now, could bring into being a small oil shale industry which would pave the way for further development, revenues and jobs in the future.

The LLNL Hot-Recycled-Solid process has the potential to improve existing oil shale technology. It processes oil shale in minutes instead of hours, reducing plant size. It processes all oil shale, including fines rejected by other processes. It provides controls to optimize product quality for different applications. It co-generates electricity to maximize useful energy output. And, it produces negligible SO_2 and NO_x emissions, a non-hazardous waste shale and uses minimal water.

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Table 1. Economics of a 10,000 Bbl/day Plant

Description	Cost & Revenue $/Bbl
Capital cost @ 15% IRR - 725 Million	$37
Unocal's projected operating costs (full production excluding hydrotreating)	$23
Hydrotreat/refine 50% into transportation fuel (cost $10/Bbl)	$5
Convert 40% to SOMAT (seasonal average - cost $5/Bbl)	$2
Convert 10% to specialty chemicals (cost $25/Bbl)	$3
Subtotal - Capital & Operating Costs	**$70**
Off-site electricity sales @ $.03/kWh	($5)
SOMAT asphalt additive @ $100/Bbl	($40)
Specialty chemicals @ $100/Bbl	($10)
Required transportation fuel price for 15% rate of return	**$30**
Transportation fuel wholesale price in 1993	**$31**

Table 2. Economics of a 50,000 Bbl/day Plant

Description	Cost & Revenue $/Bbl
Capital cost @ 15% IRR - 2,225 Million	$23
Operating costs including hydrotreating/refining	$25
Subtotal - Capital & Operating Costs	**$48**
Off-site electricity sales @ $.03/kWh	($5)
SOMAT asphalt additive 15% @ $60/Bbl	($9)
Specialty chemicals 5% @ $60/Bbl	($3)
Required transportation fuel price for 15% rate of return	**$39**